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(54) Metal hydride heat pump assembly.

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Description

The present invention relates to a metal hydride heat pump assembly according to the preamble of the patent claim.

It is known that a certain kind of metal or alloy exothermically occludes hydrogen to form a metal hydride, and the metal hydride endothermically releases hydrogen in a reversible manner. Many such metal hydrides have been known, and examples include lanthanum nickel hydride ($LaNi_5H_x$), calcium nickel hydride ($CaNi_5H_x$), misch metal nickel hydride ($M_mNi_5H_x$), iron titanium hydride ($FeTiH_x$), and magnesium nickel hydride (Mg_2NiH_x). In recent years, various heat pump devices built by utilizing the characteristics of the metal hydrides have been suggested.

Such a conventional metal hydride heat pump assembly having the features of the preamble of the patent claim is known from US—A—4 055 962. This known heat pump assembly comprises several heat pump units each comprising a first heat medium receptacle and a second heat medium receptacle. Furthermore, each pump includes a closed vessel containing a hydrogen gas atmosphere and divided into a first chamber and a second chamber. This embodiment does not have any special means for heat exchange between the first receptacle of the first heat pump unit and the first receptacle of the second heat pump unit, however, the receptacles of the one heat pump units are in direct connection with the receptacles of the other heat pump units so that these receptacles appear to be in direct heat exchange contact.

US—A—4 039 023 describes a compressor for compressing hydrogen to the required pressure for introducing the same into the core of a hydride container. However, the assembly of this reference uses only one kind of metal hydride which is put into two cores. Furthermore, this known system uses only one heat pump unit and does not have any heat exchange means comparable with the heat exchange means of the present assembly.

A metal hydride heat pump assembly having the features of the preamble of the patent claim is also described in EP—A—0 055 855 of which the present subject was divided out.

It is the object of the invention to provide a metal hydride heat pump assembly of the cited kind having an especially high coefficient of performance.

This object is achieved by a metal hydride heat pump assembly of the invention having the feature of the characterizing portion of the patent claim.

Preferred embodiments of the invention are described below with reference to the drawings in which:

Figure 1 is a rough view showing an embodiment of a heat pump assembly without compressor;

Figure 2 is a graph showing the temperature characteristics of the equilibrium dissociation pressures of metal hydrides for the purpose of illustrating the operation cycle of a heat pump assembly;

Figure 3 is a graph for illustrating a different operation cycle from that shown in Figure 2; and

Figure 4 is a diagrammatic view of another example of the heat pump assembly.

According to the metal hydride heat pump assembly as shown in Figure 1, a heat pump unit composed of a first heat medium receptacle 11, a second heat medium receptacle 14 and a plurality of closed vessels 17A, 17B, . . . is disposed in juxtaposition with another heat pump unit composed of a first heat medium receptacle 11′, a second heat medium receptacle 14′ and a plurality of closed vessels 17A′, 17B′, ... A heat exchanging means 41 is provided between the first heat medium receptacles 11 and 11′, and a heat exchanging means 42 is provided between the second heat medium receptacles 14 and 14′. The heat exchanging means 41 and 42 are composed of pumps 43 and 44 and fluid (e.g., water) conduits 45 and 46, respectively. The heat exchange may also be carried out by simply exchanging the staying heat media between the heat medium receptacles 11 and 11′ (or 14 and 14′).

When heat exchange is performed between the heat medium receptacles in the two heat pump units by means of the heat exchanging means after the transfer of hydrogen between the first and second chambers in each unit is over, the decrease of the coefficient of performance which is due to the heat capacity of the device is limited to a small extent as compared with the case of not performing such heat exchanging.

The coefficient of performance of a cooling output cycle in the device of Figure 1 without using heat exchanging means 41 and 42 is determined as follows:

The coefficient of performance can be determined from the heat balances in the individual operating steps. For simplification, let us assume that in each chamber, *m* moles of hydrogen react, the heats of reaction of M_1H and M_2H per mole of hydrogen are ΔH_1 and ΔH_2, the neat capacity of each of the chambers 19 and 19′ containing M_1H is J_1, and the heat capacity of each of the chambers 20 and 20′ containing M_2H is J_2.

(1) Step of occluding and releasing hydrogen

It is understood that in Figure 2, the chambers 19, 20, 19′ and 20′ assume the states shown by points A, B, C and D. In the chamber 19, the amount of heat, $Q_1=m\Delta H_1$, is applied by the heat medium receptacle 11 whereby M_1H at temperature T_H releases *m* moles of hydrogen. The released hydrogen enters the chamber 20 kept at temperature T_M (for example, ambient temperature) through the partitioning wall 18 and is occluded by M_2H to generate heat in an amount $Q_2=m\Delta H_2$. This amount of heat is taken away by a cooler kept at temperature T_M.

In the meantime, in the chamber 20′, M_2H releases *m* moles of hydrogen in the course of changing from point B to point D, thereby absorbing heat in an amount of $m\Delta H_2$. Since heat in an amount, $Q_3=J_2(T_M-T_L)$, is absorbed in order to cool the chamber 20′ itself from temperature T_M to temperature T_L, the chamber 20′ takes away heat in an amount $Q_4=m\Delta H_2-Q_3$ from the cooling load. Hydrogen released in this step enters the chamber 19′ through a partitioning wall 18′ and MH_1 generates heat in an amount of ΔH_1, which heat is taken away by the cooler.

(2) Step of reversal

If the heat of the atmospheric air is to be used in order to heat the chamber 20′ from temperature T_L to temperature T_M, and return M_2H from point D to point B, the thermal balance to be considered in this step is the amount of heat, $Q_5=J_1(T_H-T_M)$, which is applied to the chamber 19′ from the heat medium receptacle 11′ to heat the chamber 19′ from temperature T_M to temperature T_H and return M_1H from point C to point A.

(3) Step of hydrogen occlusion and releasing

In this step, the chamber 19′ corresponds to the chamber 19 in step (1), and the chamber 20′ to the chamber 20 in step (1). Hence, heat in an amount $Q_6=m\Delta H_1$ is supplied to the chamber 19′, and the chamber 20 takes away heat in an amount

$$Q_7=m\Delta H_2-J_2(T_M-T_L)$$

from the cooling load.

(4) Step of reversal

This step is for completing the cycle. Thus, heat in an amount $Q_8=J_1(T_H-T_M)$ is applied to the chamber 19 from the heat medium receptacle 11 in order to heat the chamber 19 from temperature T_M to temperature T_H and return MH_1 from point C to point A.

From the above analysis, the coefficient of performance COPc of the heat pump as a device for providing a cooling output is given by the following equation.

$$\mathrm{COPc}=\frac{Q_4+Q_7}{Q_1+Q_5+Q_6+Q_8}=\frac{2(m\Delta H_2-Q_3)}{2(m\Delta H_1+J_1(T_H-T_M))}=\frac{m\Delta H_2-J_2(T_M-T_L)}{m\Delta H_1+J_1(T_H-T_M)} \quad \text{(I)}$$

It is seen from the above equation that when the heat exchanging means 41 and 42 are not used, the heat capacities of the chambers which reduce the coefficient of performance are a major influencing factor.

In producing a heating output by the cycle shown in Figure 3, the chamber 20 at ordinary temperature T_L is heated to temperature T_M by a heat source kept at temperature T_M to release hydrogen. For this purpose, heat in an amount of $J_2(T_M-T_L)+m\Delta H_2$ is supplied to the chamber 20 from a heat source. The released hydrogen is occluded by M_1H at temperature T_M in the chamber 19, whereby the temperature of the chamber 19 reaches T_H. If the amount of heat required for heating the chamber 19 itself, the amount of heat supplied to the heating load is $m\Delta H_1-J_1(T_H-T_M)$. Then, the chamber 20 is cooled with the atmospheric air in order to return its temperature to T_L. Thus, the chamber 19 releases hydrogen to M_2H at temperature T_L and attains temperature T_M. If the heat generated by the hydrogen occlusion of M_2H is taken away by the atmospheric air, the amount of heat required for this operation is $m\Delta H_1-J_1(T_H-T_M)$. Since the chambers 19′ and 20′ repeat the above operation with a phase deviation of a half cycle, the coefficient of performance COP_H of this device is given by the following equation.

$$COP_H=\frac{m\Delta H_1-J_1(T_H-T_M)}{m(\Delta H_1+\Delta H_2)-J_1(T_H-T_M)+J_2(T_M-T_L)} \quad \text{(II)}$$

In this case, too, it is seen that the heat capacities of the chambers reduce the coefficient of performance of the device.

When the device of Figure 1 is operated as described hereinabove by using the heat exchanging means 41 and 42, the coefficient of performance of the device is determined in the following manner.

For simplicity, the same conditions as given hereinabove are used, and it is to be understood that the starting point of the operating cycle is when the chambers 19, 20, 19′ and 20′ are respectively at points C, D, A and B in Figure 2 and the transfer of hydrogen has been completed.

(1) Step of heat exchange between the chambers

The chamber 19′ is heated by means of the heat medium receptacle 11′ and kept at temperature T_H, and the chamber 19 is cooled to temperature T_M by the heat medium receptacle 11. The heating and cooling of the chambers are stopped, and a pump 43 in a heat exchanging circuit 45 is driven to perform heat exchange between the chambers 19 and 19′. As a result, the chamber 19 is heated to temperature T_F, and the chamber 19′ is cooled to temperature T_E. In other words, M_1H in the chamber 19 changes from point C

to point F, and M_1H in the chamber 19', from point A to point E. T_O in Figure 8 is the temperature which the chambers 19 and 19' would have if heat ecchange has been completely done between the chambers 19 and 19', and point O represents the state of M_1H corresponding to this temperature. Likewise, heat exchange is performed by means of a heat exchanging circuit 46 between the chamber 20 kept at temperature T_L and the chamber 20' kept at temperature T_M. As a result, the chamber 20 is heated to temperature T_K, and the chamber 20' is cooled to temperature T_G. In other words, M_2H in the chamber 20 and M_2H in the chamber 20' change from points D and B to points K and G, respectively. $T_{O'}$ in Figure 2 is the temperature which the chambers 20 and 20' would have if heat exchange has been performed completely between these chambers, and point O' represents the state of M_2H corresponding to this temperature. For simplicity, if the following relation holds good among the temperatures T_E, T_O, T_F, T_G, $T_{O'}$ and T_K, the value of this equation means the heat exchanging efficiency of the heat exchangers 41 and 42.

$$\eta=\frac{T_H-T_E}{T_H-T_O}=\frac{T_F-T_M}{T_O-T_M}=\frac{T_M-T_G}{T_M-T_{O'}}=\frac{T_K-T_L}{T_{O'}-T_L}$$

Assuming that

$$T_O=\frac{T_H+T_M}{2} \quad \text{and} \quad T_{O'}=\frac{T_M+T_L}{2},$$

then

$$T_F=T_M+\frac{\eta(T_H-T_M)}{2} \quad \text{and} \quad T_G=T_M-\frac{\eta(T_M-T_L)}{2}$$

(2) Step of heating and cooling the chambers

The operation of the pump 43 and the heat exchanging operation are stopped, and the chamber 19 is heated from temperature T_F to temperature T_H by means of the heat medium receptacle 11 whereby M_1H changes from point F to point A. The amount of heat, $Q_{11}=J_1(T_H-T_F)$, required for this heating is supplied to the chamber 19 from the heat medium receptacle 11. In the meantime, the chamber 19' is cooled from temperature T_E to temperature T_M by means of the heat medium receptacle 11' after stopping the operation of the pump 44 and the heat exchanging operation between the chambers.

(3) Step of hydrogen occlusion and releasing

While the chambers 19 are maintained at temperature T_H, and the chambers 19', at temperature T_M, *m* moles of hydrogen released endothermically from M_1H in the chambers 19 is caused to flow into the chambers 20 at temperature T_K, and simultaneously, *m* moles of hydrogen released from M_2H in the chambers 20' at temperature T_G is caused to flow into the chambers 19' kept at temperature T_M. Accordingly, heat in an amount $Q_{12}=m\Delta H_1$ is applied to the chambers 19 from the heat source, and conversely M_2H in the chambers 20 exothermically occludes hydrogen. Consequently, heat in an amount of $m\Delta H_2$ is generated, and the temperature rises from T_K to T_M. Afterward, the temperature of the chambers 20 is maintained at T_M by means of the heat medium receptacle 14.

On the other hand, the chambers 20' endothermically releases *m* moles of hydrogen and absorbs heat in an amount of $m\Delta H_2$, as stated hereinabove. When the chambers 20' themselves absorb heat in an amount of $J_2(T_G-T_L)$ and attain the temperature T_L, these chambers take away heat in an amount of

$$Q_{13}=m\Delta H_2-J_2(T_G-T_L)$$

from a cooling load through the heat medium receptacle 14'.

A half of one cycle is thus over. In the latter half cycle, the same operation is repeated in the different chambers. Thus, the coefficient of performance COP_C of this device is given by the following equation.

$$COP_C=\frac{2Q_{13}}{2(Q_{11}+Q_{12})}=\frac{m\Delta H_2-J_2(T_O-T_L)}{m\Delta H_1+J_1(T_H-T_F)}=\frac{m\Delta H_2-J_2(T_M-T_L)(1-\eta/2)}{m\Delta H_1+J_1(T_H-T_M)(1-\eta/2)} \quad \text{(III)}$$

Likewise, the coefficient of performance COP_H in a heating output cycle is given by the following equation.

$$COP_H=\frac{m\Delta H_1-J_1(T_H-T_M)(1-\eta/2)}{m(\Delta H_1+\Delta H_2)-\{J_1(T_H-T_M)-J_2(T_M-T_L)\}(1-\eta/2)} \quad \text{(IV)}$$

Hence, in the case of using the heat exchanging means 41 and 42, the proportion of the heat capacities of the chambers in the coefficient of performance is reduced by one-half of η as compared with the case of not using them. In particular, in the cooling output cycle, the coefficient of performance increases markedly.

In the metal hydride heat pump assembly as described above, a compressor (not shown in Figure 1) which pressurizes hydrogen gas in one of the first and second chambers which communicate with each other and reduces the pressure of hydrogen gas in the other is used as a means for moving hydrogen between the first and second chambers.

One example of a heat pump assembly including such a compressor is diagrammatically shown in Figure 4. In Figure 4, the first chamber 19 and the second chamber 20 are connected by means of an ordinary communicating pipe 111 and a communicating pipe 112 equipped with a compressor P_1. V_1 and V_2 represent values for the communicating pipes 111 and 112, respectively. Heat exchange between the chambers 19 and 20 is performed by means of heat media 103, 104 and 105 maintained at temperatures T_H, T_M and T_L respectively. V_3, V_4, V_5 and V_6 respectively represent valves for the heat media. P_3 and P_4 represent pumps for the heat media.

It is to be understood that Figure 4 is a simplified view and each of the chambers 19 and 20 in fact represents a plurality of chambers, and a plurality of chambers 19 and a plurality of chambers 20 are located within separate heat medium receptacles. While flowing through the heat medium receptacles, the heat media 103, 104 and 105 exchange heat with M_1H of the chambers 19 or M_2H of the chambers 20 through the walls of the chambers 19 or 20.

By using the heat pump shown in Figure 4, it is possible to move the hydrogen gas forcibly by the compressor to cause the metal hydride in one chamber to occlude hydrogen, take out the resulting heat output by the heat medium 103, cause the metal hydride in the other chamber to release hydrogen, and take out the resulting cooling output by the heat medium 105. The communicating pipe 111 is used to return hydrogen residing deviatingly in one of the chambers, and the heat medium 104 (e.g., to be supplied from the outer atmosphere) can be used to cool or heat the closed vessels and the heat medium receptacles when hydrogen transfer by means of the compressor has been completed.

Claim

A metal hydride heat pump assembly comprising a first and a second heat pump unit, each of said heat pump units comprising a first heat medium receptacle (11, 11'), having heat medium flowing therein, a second heat medium receptable (14, 14') having heat medium flowing therein, and at least one closed vessel (17a, 17b; 17a', 17b') containing a hydrogen gas atmosphere and divided into a first chamber (19, 19') having a first metal hydride (M_1H) filled therein and a second chamber (20, 20') having a second different metal hydride (M_2H) filled therein, said first and second chambers (19, 19', 20, 20') of said closed vessel being made to communicate with each other so that hydrogen gas passes from one chamber to the other but the metal hydrides do not, said first chamber (19, 19') of the closed vessel being located within the first heat medium receptacle (11, 11') and said second chamber (20, 20') of the closed vessel being located within the second heat medium receptacle (14, 14'), whereby heat exchange is carried out between heat media in the first and second heat medium receptacles (11, 11', 14, 14') and the first and second metal hydrides through the external walls of the closed vessels, and further comprising means (41) for heat exchange between the first heat medium receptacle (11) of the first heat pump unit and the first heat medium receptacle (11') of the second heat pump unit, means (42) for heat exchange between the second heat medium receptable (14) of the first heat pump unit and the second heat medium receptacle (14') of the second heat pump unit, characterized in that it comprises a compressor (P_1) for forcing hydrogen gas from one chamber (20, 20') to the other chamber (19, 19') in said at least one closed vessel (17a, 17b; 17a', 17b').

Patentanspruch

Metallhydrid-Wärmepumpenanordnung mit einer ersten und einer zweiten Wärmepumpeneinheit, von denen jede einen ersten Wärmemedium-Behälter (11, 11'), in dem ein Wärmemedium strömt, einen zweiten Wärmemedium-Behälter (14, 14'), in dem ein Wärmemedium strömt und zumindest ein geschlossenes Behältnis (17a, 17b; 17a', 17b') hat, das eine Wasserstoffgasatmosphäre enthält und in eine erste Kammer (19, 19') mit einem darin eingefüllten ersten Metallhydrid (M_1H) und in eine zweite Kammer (20, 20') mit einem anderen darin eingefüllten zweiten Metallhydrid (M_2H) unterteilt ist, wobei die erste und zweite Kammer (19, 19'; 20, 20') des geschlossenen Behältnisses derart untereinander verbunden sind, daß das Wasserstoffgas aber nicht die Metallhydride von einer Kammer in die andere Kammer übertreten; die erste Kammer (19, 19') des geschlossenen Behältnisses ist innerhalb des ersten Wärmemedium-Behälters (11, 11') und die zweite Kammer (20, 20') des geschlossenen Behältnisses ist innerhalb des zweiten Wärmemedium-Behälters (14, 14') angeordnet, wobei der Wärmeaustausch zwischen den sich in der ersten und zweiten Wärmemedium-Behältern (11, 11'; 14, 14') befindlichen Wärmemedien und den ersten und zweiten Metallhydriden durch die Außenwände der geschlossenen Behältnisse stattfindet und die Metallhydrid - Wärmepumpenanordnung hat darüberhinaus Einrichtungen (41) zum Wärmeaustausch zwischen dem ersten Wärmemedium-Behälter (11) der ersten Wärmepumpeneinheit und dem ersten

Wärmemedium-Behälter (11′) der zweiten Wärmepumpeneinheit, Einrichtungen (42) zum Wärmeaustausch zwischen dem zweiten Wärmemedium-Behälter (14) der ersten Wärmepumpeneinheit und dem zweiten Wärmemedium-Behälter (14′) der zweiten Wärmepumpeneinheit, gekennzeichnet durch einen Kompressor (P1) mit dem Wasserstoffgas von einer Kammer (20, 20′) in die andere Kammer (19, 19′) des zumindest einmal vorhandenen geschlossenen Behältnisses (17a, 17b; 17a′, 17b′) gepumpt wird.

Revendication

Un assemblage de pompe à chaleur à hydrure métallique comprenant une première et une seconde unité de pompe à chaleur, chacune desdites unités de pompe comprenant un premier récipient de fluide thermique (11, 11′), présentant dans celui-ci un écoulement de fluide thermique, un second récipient de fluide thermique (14, 14′) présentant dans celui-ci un écoulement de fluide thermique, et au moins une curve fermée (17a, 17b; 17a′, 17b′) contenant une atmosphère d'hydrogène gazeux et divisée en une première chambre (19, 19′) contenant un premier hydrure métallique (H_1H) en son sein et une seconde chambre (20, 20′) contenant un second hydrure métallique différent (H_2H) en son sein, lesdites première et seconde chambres (19, 19′, 20, 20′) de ladite curve fermée étant conçues pour communiquer entre elles de façon à ce que l'hydrogène gazeux passe d'une chambre à l'autre mais pas les hydrures métalliques, ladite première chambre (19, 19′) de la cuve fermée étant située dans le premier récipient à fluide thermique (11, 11′) et ladite seconde chambre (20, 20′) de la cuve fermée étant située dans le second récipient à fluide thermique (14, 14′), ce qui fait que l'échange de chaleur est effectué entre les fluides thermiques dans les premier et second récipients à fluide thermique (11, 11′, 14, 14′) et les premier et second hydrures métalliques à travers les parois extérieures des cuves fermées, et comprenant en outre des moyens (41) pour réaliser l'échange de chaleur entre le premier récipient à fluide thermique (11) de la première unité de pompe à chaleur et le premier récipient à fluide thermique (11′) de la seconde unité de pompe à chaleur, des moyens (42) pour l'échange de chaleur entre le second récipient à fluide thermique (14) de la première unité de pompe à chaleur et le second récipient à fluide thermique (14′) de la seconde unité de pompe à chaleur, caractérisé en ce qu'il comprend un compresseur (P_1) pour forcer l'hydrogène gazeux à passer d'une chambre (20, 20′) à l'autre chambre (19, 19′) dans ladite au moins une cuve fermée (17a, 17b; 17a′, 17b′).

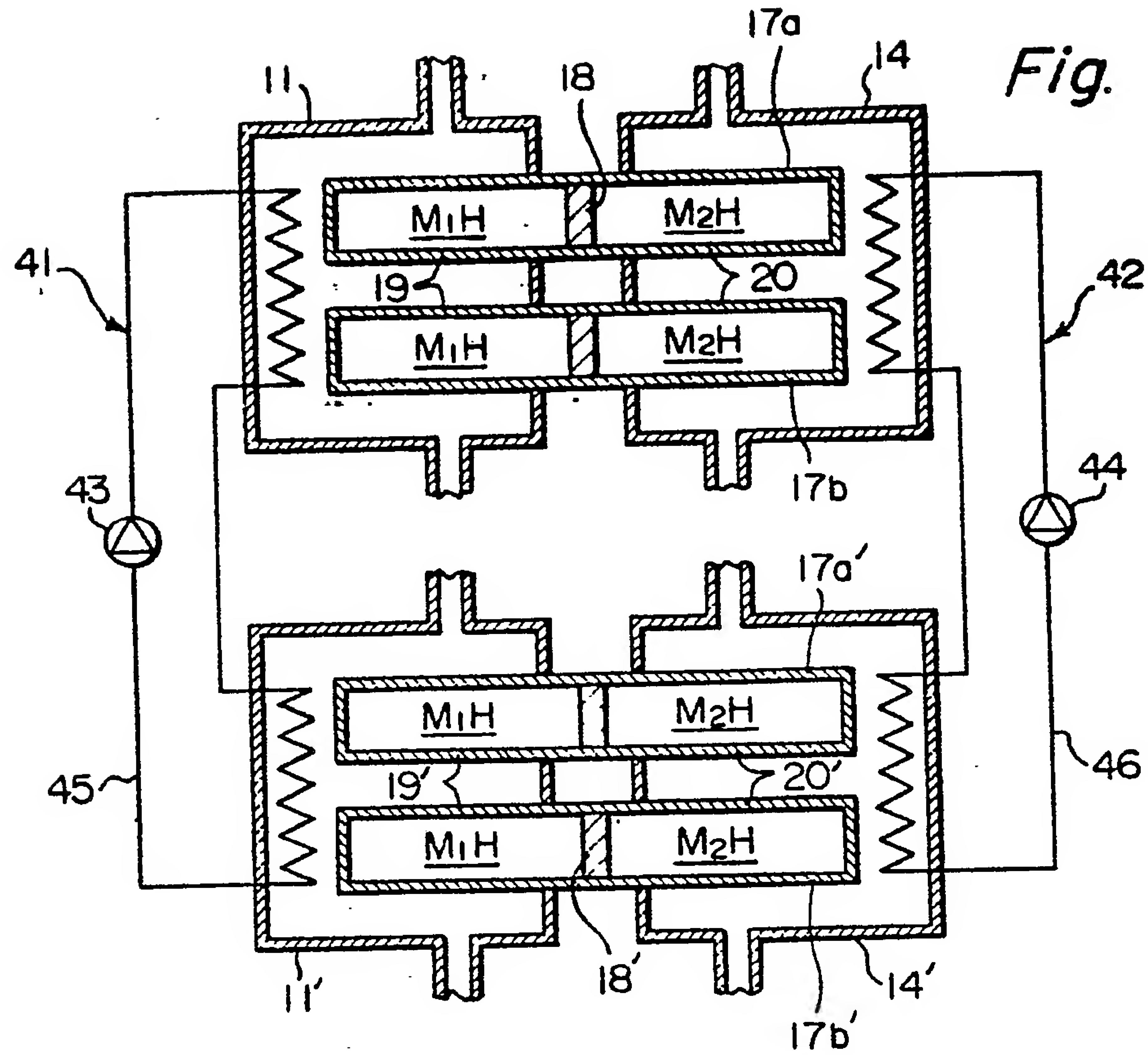

11
18
17a
14
41
19
20
42
M1H
M2H
43
44
17b
17a'
45
19'
20'
46
11'
18'
14'
17b'

Fig. 1

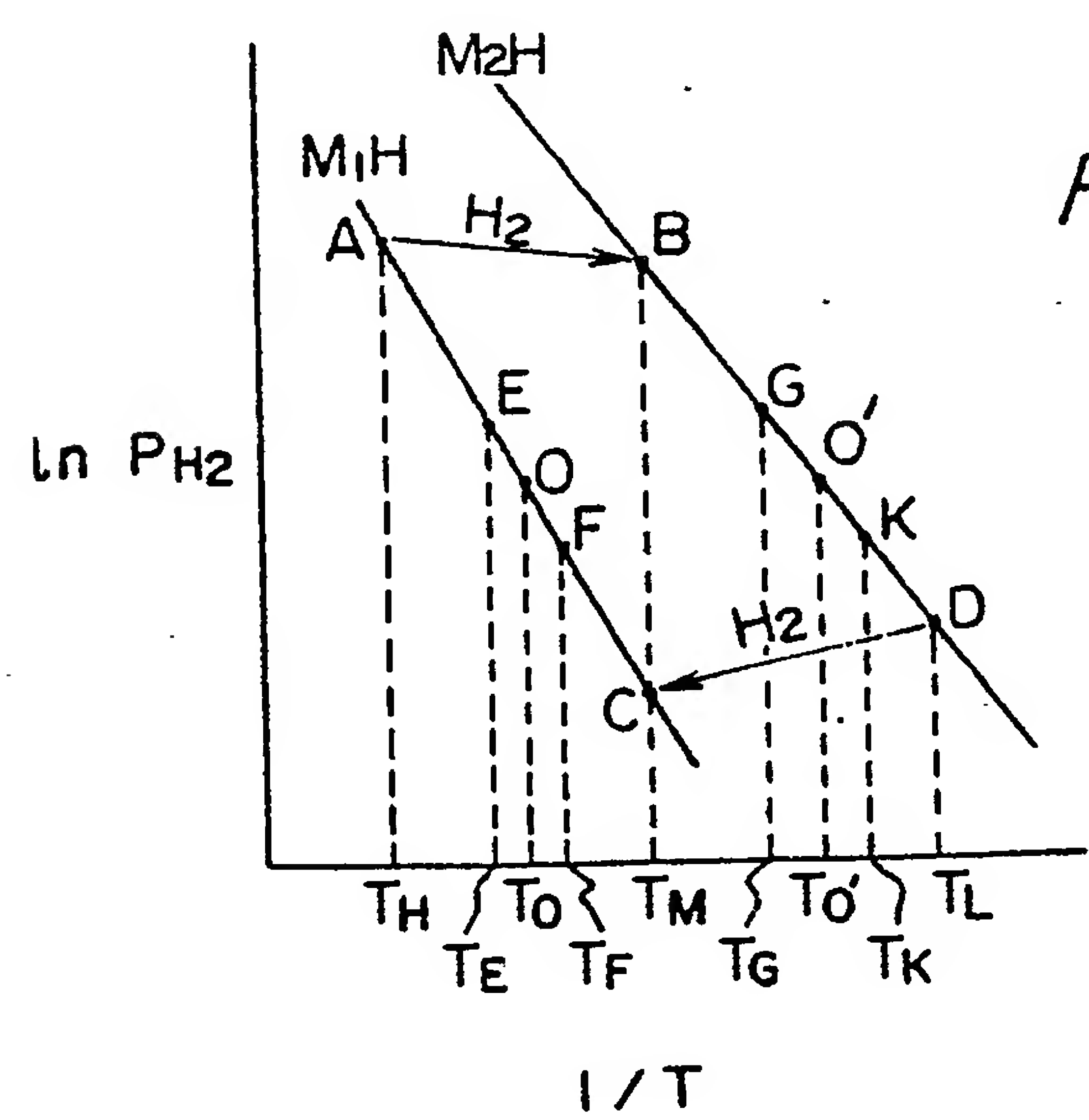
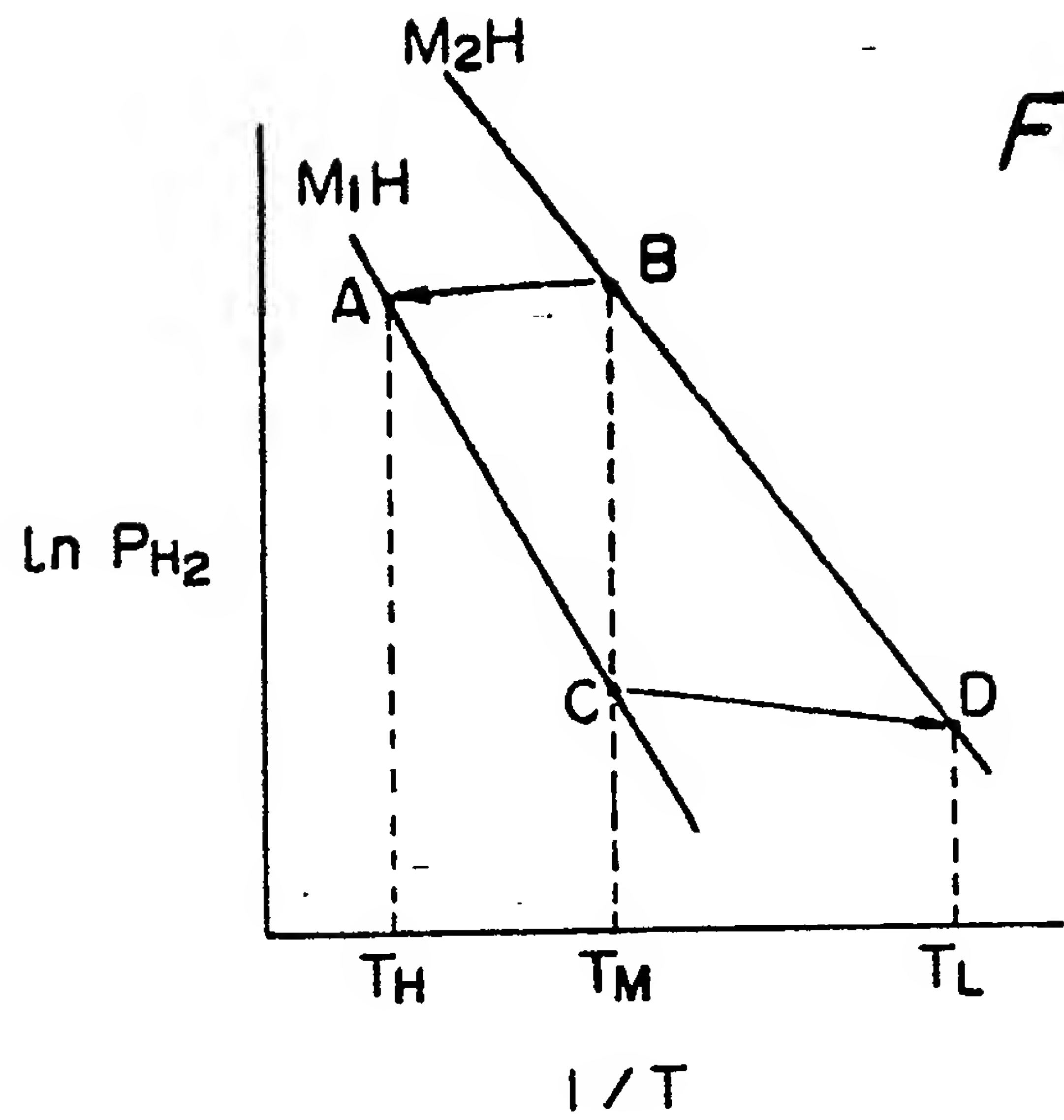

M2H
M1H
A
H2
B
E
G
O'
ln PH2
O
K
F
D
H2
C
TH
TE
TO
TF
TM
TG
TO'
TK
TL
1/T

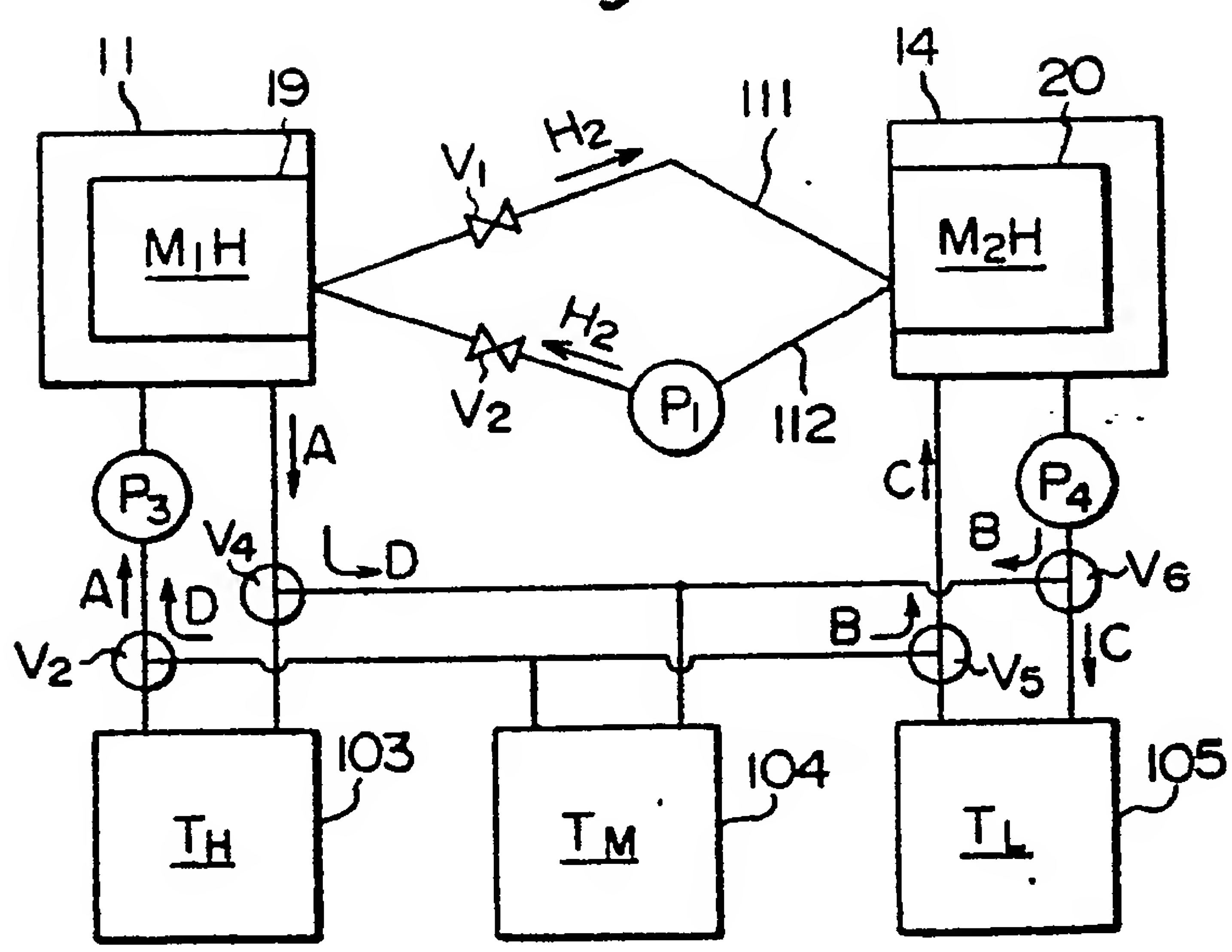
Fig. 2



M2H
M1H
A
B
C
D
Ln PH2
TH
TM
TL
1 / T

Fig. 3

Fig. 4



11
19
M1H
V1
H2
111
14
20
M2H
H2
V2
P1
112
P3
A
V4
D
C
P4
B
V6
A
D
V2
B
V5
C
103
104
105
TH
TM
TL